

IONIC EQUILIBRIUM-I

Structure

7.1	Introduction	7.4	Theories of Acids and Bases: A Review
	Expected Learning Outcomes		
7.2	Electrolytes and Non-Electrolytes		Arrhenius Theory
	Strong and Weak Electrolytes		Bronsted and Lowry Theory
	Degree of Ionisation	7.5	Lewis Theory
	Factors Affecting Degree of Ionisation of Weak Electrolytes		Ionic Product of Water, K_w
7.3	Ionisation Constant and Ostwald's Dilution Law	7.5	pH Scale
	Ostwald's Dilution law		Calculation of pH
		7.6	Summary
		7.7	Terminal Questions
		7.8	Answers

7.1 INTRODUCTION

In the previous two units of this block you have learnt about general aspects of Chemical Equilibrium in terms of its types, significance, representation and factors affecting it etc. As you know that a large number of the reactions in the general chemistry laboratory are carried out in aqueous solutions and many of these contain ionic species. The equilibrium in such systems containing ionic species is referred to as Ionic Equilibrium and is the topic of this and the next two units. We would apply the concepts learnt in the previous two units to the systems having ionic species.

We would begin the unit by taking up the nature of aqueous solutions in terms of their electrical conductivity based on the nature of the solute. In this context you would learn about electrolytes, their types and the factors affecting their behaviour. We would also talk about the ionisation equilibrium of weak electrolytes, its characterisation in terms of ionisation constant, and Ostwald's dilution law. This would be followed by a review of different theories of acids and bases, as these constitute a significant class of substances showing ionic equilibrium. Herein, we would take up different theories and learn about their

merits and demerits. Towards the end of the unit, we would take up the discussion on autoprotolysis—an important property of water. In this context we would define ionic product of water and discuss its significance. We would then define the concept of pH and take up some examples for the calculation of pH value of solutions of strong acids and bases.

In the next unit, you would learn about equilibria in the aqueous solutions of weak acids/bases, polyprotic acids and mixtures of weak acids/bases with salts containing common ions.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define and differentiate between electrolytes and non-electrolytes;
- ❖ define degree of ionisation of a weak electrolyte and discuss the factors affecting it;
- ❖ state and explain Ostwald's dilution law;
- ❖ describe different theories of acids and bases;
- ❖ state the merits and limitations of different theories of acids and bases;
- ❖ define conjugate acid-base pairs and identify them in an acid-base equilibrium;
- ❖ define ionic product of water and explain its significance; and
- ❖ define pH and calculate the same for aqueous solutions of strong acids and bases.

7.2 ELECTROLYTES AND NON-ELECTROLYTES

You must be aware that one should not operate electrical equipment with wet hands or while standing in water. Have you ever thought that why are we advised so? This is due to the conducting nature of water from tap, river or pond or so. As a consequence of conducting nature of water, the electric current may flow from the electrical appliance to the human body and the person operating the electrical appliance with wet hands may get electrocuted. Now, the question is what makes water conducting? In fact, the pure water is practically non-conducting; it is the presence of the ionic species in the water that makes it conducting. Let us learn about the behaviour of aqueous solutions that contain ionic species.

A wide variety of aqueous solutions are electrically conducting in nature. The conducting nature of the solution is determined by the nature of the solute dissolved in water. For example, suppose we take two beakers containing say 100 cm^3 of distilled water each and to one of these beakers we add 2 g of sugar whereas to the second beaker we add 2 g of sodium chloride. The solution of sugar in water is found to be non-conducting whereas that of sodium chloride is observed to be conducting. The solutes whose aqueous

An electrolyte is a substance that dissolves in water to give an electrically conducting solution

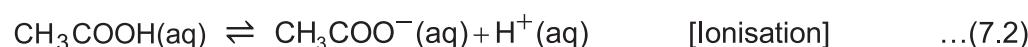
solutions conduct electricity are called **electrolytes** and the ones whose aqueous solutions do not conduct electricity are called **non-electrolytes**. Swedish Chemist Svante' Arrhenius explained the conductivity of aqueous solutions in terms of the *ionic theory of solutions*. He proposed that certain substances when dissolved in water produce freely moving ions, which are responsible for conducting nature of aqueous solutions.

Let us analyse the example given above. To begin with, a sample of water consists of a large number of water molecules, which are polar but electrically neutral and are extensively hydrogen bonded. The water molecules do not carry any net electric charge, so when they move no overall electric charge is carried and for all practical purposes water is non-conducting. However, when a substance like sodium chloride dissolves in water, the crystal lattice of sodium chloride is broken and sodium ions and chloride ions are released in the solution. These ions move under the influence of an electric field towards the oppositely charged electrodes. Each ion carries a certain quantity of charge and contributes towards electrical conductivity. On the other hand, when we dissolve sugar in water, the intermolecular interactions between the sugar molecules are broken and *neutral* sugar molecules are released in the solution. As the sugar molecules do not carry any charge and when they move no charge is carried and as a result the solution is non-conducting.

7.2.1 Strong and Weak Electrolytes

Let's take our argument further and raise a question that, "are the solutions of all electrolytes equally conducting?" To answer this question, let's once again take two beakers. In one of these we take 0.01 M solution of sodium chloride whereas in the other we take 0.01 M solution of acetic acid. Both of these are electrolytes i.e., their solutions conduct electricity but it is found that their equimolar solutions conduct electricity to different extents. The aqueous solution of acetic acid is poorly conducting whereas that of sodium chloride is highly conducting. How do we explain this?

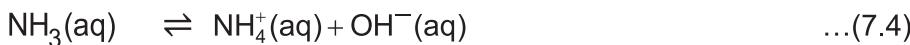
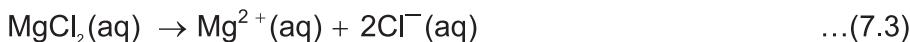
You would recall from above, that Arrhenius explained the electrical conductivity of aqueous solutions in terms of presence of ions in the solution. As both the solutions taken in the example given above, have same molar concentration we expect similar number of ions in solutions and hence similar conductivities. The difference in their electrical conductivities is due to the fact that in case of sodium chloride, the electrolyte is completely dissociated into its ions whereas in case of acetic acid only a few ions are generated in the solution due to the ionisation. An aqueous solution of acetic acid consists mainly of unionised acetic acid molecules and only some acetate ions and hydrogen ions generated by ionisation of a few acetic acid molecules depending on its concentration. The electrolytes like NaCl, which completely dissociate in aqueous solutions, are called **strong electrolytes** whereas the ones which are partially ionised are called **weak electrolytes**. The generation of ions in the two cases can be represented as



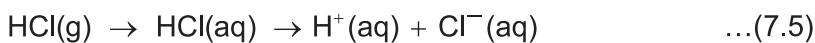
You may have noticed that we have used two terms viz., dissociation and ionisation in our discussion above. Though these are used interchangeably we need to understand the difference between them. When the electrolyte is ionic i.e., consists of ions as in NaCl crystal we use the term **dissociation** to convey that the ions in the crystal are *dissociated* from each other and are released in the solution. On the other hand, if the electrolyte is a molecular species as in acetic acid we use the term **ionisation** to convey that the molecular electrolyte *ionises* to produce ions in the solution. *In one case the ions are already there and get dissociated whereas in the other case the ions are generated in solution.*

An ionic compound produces ions in aqueous solution by dissociation whereas a molecular compound produces ions in solution by ionisation.

Let's take one more example. Let's again take two beakers containing 0.01 M solutions of magnesium chloride and ammonia respectively. We find that the solution of magnesium chloride is highly conducting whereas that of ammonia has relatively much lower electrical conductivity. This indicates that while ionic compound, magnesium chloride is a strong electrolyte; molecular ammonia is an example of a weak electrolyte. The process of generation of ions in the two cases can be represented as



On the basis of the examples of electrolytes taken above, we may conclude that *generally molecular compounds are either nonelectrolytes (cf. sugar) or weak electrolytes (cf. acetic acid) whereas ionic compounds (cf. NaCl and MgCl₂) are strong electrolytes*. However, there are exceptions, for example if we dissolve a molecular compound, HCl (g) in water we get a highly conducting solution. Hydrogen chloride gas is dissolved in water; it gives HCl (aq), which is a strong electrolyte that ionises completely in solution to produces hydrogen ions and chloride ions.



You may note that in case of acetic acid and ammonia we used double arrow to indicate partial ionisation and equilibrium between ionised and unionised species whereas in case of hydrochloric acid we have used a single arrow to convey that there is complete ionisation.

Generally molecular compounds are either nonelectrolytes or weak electrolytes whereas ionic compounds are strong electrolytes.

7.2.2 Degree of Ionisation

Let's move on and raise another question, "Will two weak electrolytes have same electrical conductivity?" To find answer, we take 0.001 M solutions of acetic acid and chloroacetic acid in two different beakers and measure their electrical conductivities. We find that the electrical conductivity of chloroacetic acid is much more than that of acetic acid. A calculation, about which you would learn in the next unit, shows that in case of 0.001 M chloroacetic acid there are approximately 8.8 times more ions than in a solution of acetic acid of same concentration. It means that chloroacetic acid is more ionised than acetic acid and hence has more electrical conductivity.

The extent of ionisation of a weak electrolyte is quantified or expressed in terms of **degree of ionisation** (also called as **degree of dissociation**). It is indicated by a symbol ‘ α ’ and refers to the fraction of molecules of the weak electrolyte that give ions in solution. In other words, it may be seen as the ratio of the number of ionised electrolyte molecules to the total number of the electrolyte molecules dissolved in water.

Degree of ionisation

$$= \frac{\text{Number of molecules of electrolyte ionised}}{\text{Total number of molecules of electrolyte dissolved}} \quad \dots(7.6)$$

Sometimes the extent of ionisation is expressed as percentage ionisation. It is obtained by multiplying the degree of ionisation by 100.

Percentage ionisation

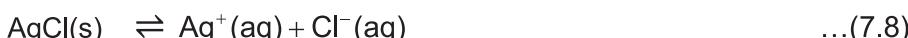
$$= \frac{\text{Number of molecules of electrolyte ionised}}{\text{Total number of molecules of electrolyte dissolved}} \times 100 \% \quad \dots(7.7)$$

Let's learn about the factors affecting the degree of ionisation of weak electrolytes.

7.2.3 Factors Affecting Degree of Ionisation of Weak Electrolytes

The strong electrolytes by definition are fully ionised in solution i.e., their degree of ionisation is 1. However, the degree of ionisation of a weak electrolyte is much less than 1 and depends on a number of factors as discussed below.

- i) **Nature of solvent:** the nature of solvent is an important factor that determines the degree of ionisation of an electrolyte. A solvent of high dielectric constant has higher ionising power and is favorable for the ionisation of the electrolyte. Water with highest dielectric constant is the best ionising solvent available.
- ii) **Temperature:** the degree of ionisation increases with an increase in the temperature of the solution. That means at higher temperature there is higher ionisation of the weak electrolyte. This can be understood in terms of the effect of temperature on ionisation equilibrium constant about which you would learn later.
- iii) **Presence of common ions:** the degree of ionisation of weak electrolytes is affected by the presence of a strong electrolyte having an ion common to the ions obtained from ionisation of the electrolyte. This can be rationalised in terms of the effect of addition of a common ion (product) to a reaction at equilibrium (Le- Chatelier's principle). For example, the solubility of sparingly soluble AgCl decreases further in presence of NaCl that provides common Cl⁻ ions.



The Cl^- ions obtained from the ionisation of NaCl shift the solubility equilibrium of AgCl in the backward direction and decrease the solubility of AgCl . You would learn about it in details in Unit 9.

- iv) **Dilution:** the degree of ionisation of a weak electrolyte increases with dilution. In order to understand the effect of dilution we need to learn about ionisation constant and the Ostwald's dilution law, which we would take up in the next section.

However, before proceeding further, answer the following simple question to assess your learning.

SAQ 1

Explain the difference between dissociation and ionisation with the help of suitable examples.

7.3 IONISATION CONSTANT AND OSTWALD'S DILUTION LAW

You have learnt that a weak electrolyte is partially ionised in aqueous solutions and there is equilibrium between the ionised and unionised species. In order to understand the process, let us take a weak molecular electrolyte, AB that ionises to give A^+ and B^- ions. To begin with, some molecules of AB ionise to give the ions, which is followed by recombination of some of the ions to give back unionised molecular electrolyte. The process continues till there is equilibrium between the unionised electrolyte and the ions. The ionisation equilibrium can be represented as



At a given temperature, the relative proportions of ionised and unionised forms of the electrolyte (AB) remain fixed at equilibrium with unionised AB molecules being the predominant species. The equilibrium can be characterised in terms of the equilibrium constant as given below.

$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} \quad \dots(7.11)$$

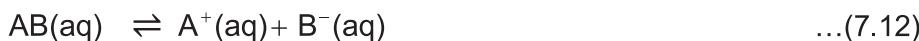
As the equilibrium constant characterises an ionisation (or dissociation) reaction it is called **ionisation (or dissociation) constant**. The magnitude of ionisation constant depends on the degree or extent of ionisation of the electrolyte; higher the ionisation, higher is the magnitude of ionisation constant.

7.3.1 Ostwald's Dilution Law

In the process of studying the chemical affinities of acids and bases Wilhelm Ostwald applied (in 1888) the law of mass action to the ionisation of weak acids, and developed a simple mathematical relationship between the degree

of dissociation (α), the concentration (c), and the equilibrium constant (K) for the dissociation of weak acids. This relationship is known as the **Ostwald's dilution law** and is valid for weak electrolytes. The relationship can be derived as follows.

Let us consider a weak electrolyte, AB that ionizes partially to give A^+ and B^- ions and the equilibrium between ionised and unionised species in the solution can be represented as



If we begin with $c \text{ mol dm}^{-3}$ of the electrolyte and assume that the degree of ionisation (or dissociation) is ' α ' then the concentration of various species in the solution in the beginning and at the equilibrium can be represented as

	AB (aq) \rightleftharpoons	$A^+(aq)$	$+ B^-(aq)$
Initial concentration	c	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
Equilibrium concentration	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the reaction can be written as

$$K = \frac{[A^+][B^-]}{[AB]} \quad \dots(7.13)$$

Substituting the concentrations of various species at equilibrium in the equilibrium constant expression Eq. (7.13), we get

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(7.14)$$

Since, for weak electrolytes, $\alpha \ll 1$, we can ignore α in the denominator and write

$$K = c\alpha^2 \quad \dots(7.15)$$

Rearranging and solving, we get,

$$\alpha = \sqrt{\frac{K}{c}} \quad \dots(7.16)$$

As $c\alpha = \frac{1}{V}$ where V is the volume of the solution containing a certain amount of solute; V , increases with dilution,

We can write,

$$\alpha = \sqrt{KV} = K' \sqrt{V} = \frac{K'}{\sqrt{c}} \therefore K' = \sqrt{K} \quad \dots(7.17)$$

This is the mathematical expression for **Ostwald's dilution law** and implies that, “*The degree of ionisation of a weak electrolyte is directly proportional to the square root of dilution or inversely proportional to the square root of the concentration*”

The Ostwald dilution law can be experimentally verified by determining the degree of ionisation for a weak electrolyte at different dilutions using conductance measurements. The degree of ionisation is determined as a ratio of the conductance of the electrolyte at a given dilution to its conductance at infinite dilution.

$$\alpha = \frac{\lambda_V}{\lambda_\infty} \quad \dots(7.18)$$

Where, λ_V and λ_∞ are the equivalent conductances at dilution V and infinite dilution respectively. You may note here that this law is not valid for strong electrolytes because the *strong electrolytes ionise completely at all dilutions*. To assess whether you have understood Ostwald's law, solve the following question.

Strong electrolytes
ionise completely at
all dilutions

SAQ 2

State and explain Ostwald's dilution law.

7.4 THEORIES OF ACIDS AND BASES: A REVIEW

In your earlier classes you must have studied about acids and bases. You may also be aware that there are different theories of acids and bases. As we are going to take up the equilibria involving acids and bases in aqueous solutions, it is worthwhile to recall the basic theories of acids and bases.

7.4.1 Arrhenius Theory

It is the earliest and most commonly used theory of acids and bases. It was proposed by Svante' Arrhenius in 1884 while explaining the electrical properties of solutions of electrolytes. Prior to 1884, it was believed that the passage of electrical current through the solutions of some substances generates charged species called ions that are responsible for the electrical conductivity of the solutions. Contrary to this belief, Arrhenius proposed that the passage of electrical current is not essential for the conducting properties of solutions of electrolytes; these substances when dissolved in water dissociate into ions and conduct electricity. Acids and bases are examples of such substances. Arrhenius defined an acid as a substance that produces hydrogen ions (H^+) by dissociating in aqueous solution. According to Arrhenius, the dissociation reaction for an acid, HA can be represented as



Where A^- refers to the anion of the acid. Similarly, an acid HX would dissociate as



Modern investigations reveal that the hydrogen ion may bind with as many as four water molecules and exist as H_9O_4^+ (aq)

Arrhenius was awarded the 1903 Nobel Prize in Chemistry, "in recognition of the extraordinary services he has rendered to the advancement of Chemistry by his electrolytic theory of dissociation."

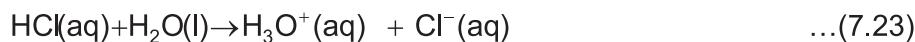
The generation of H^+ ion in all acid solutions explains the similarity of the properties of all acids. Hydrochloric acid, HCl is an example of an Arrhenius acid whose dissociation can be represented as



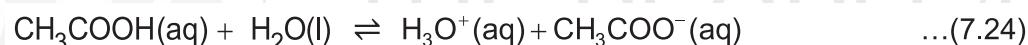
It is however, worthwhile to note here that the hydrogen ions so produced in aqueous solutions cannot exist independently; these combine with the water molecules in the solution. It is due to the fact that the hydrogen ions are very small in size ($\sim 10^{-15}$ m) and each hydrogen ion carries one unit of positive charge. The consequent high charge density (charge / size) makes it impossible for the H^+ ion to exist free in a polar solvent like water. Therefore, it binds itself to a water molecule and forms H_3O^+ ion called **hydronium ion** (or oxonium ion or the hydroxonium ion) as given below.



The ionisation of HCl in water may then be represented as



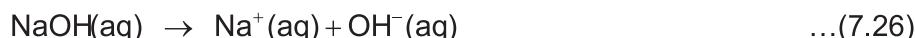
Therefore, according to the modern view of the Arrhenius concept an acid may also be defined as a substance that, when dissolved in water, produces hydronium ions, H_3O^+ (aq). It is worthwhile to make a mention of another class of molecules that increase the concentration of hydronium ions on being dissolved in water. These ionise to generate hydronium ion, e.g., acetic acid. The ionisation of acetic acid can be represented as



Such acids are called as **weak acids**. You would learn in details about weak acids in the next unit. On the other hand, according to Arrhenius, a base is defined as a substance that produces a hydroxide ion (OH^-) on dissociation in aqueous solutions.



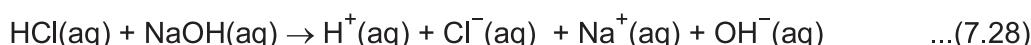
Where M^+ refers to the cation of the base. Sodium hydroxide is a common example of an Arrhenius base, dissociating as,

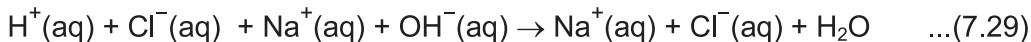


Similar to weak acids, certain molecules behave as weak bases and produce hydroxide ions on ionisation. For example, the ionisation of a weak base, ammonium hydroxide can be represented as



The neutralisation reaction between a strong acid (say HCl) and a strong base (say NaOH) can be represented as





Cancelling common terms in Eq.(7.29) we get



As can be seen above, Eq. (7.29), the Na^+ and Cl^- ions do not participate in the neutralisation reaction. Such ions are called as **spectator ions**. Thus, the neutralisation reaction between a strong acid and a strong base, according to Arrhenius theory, is basically the reaction between a hydrogen ion and a hydroxide ion to give a molecule of water. Thus, we see that the Arrhenius theory is quite simple and explains the acid-base behaviour of substances to a good extent. However it has a few limitations like:

- It is applicable for aqueous solutions only.
- It does not explain the acidic behaviour of some substances that lack hydrogen (e.g., AlCl_3 , SO_3 , N_2O_5) or the basic character of substances that lack OH (e.g., NH_3 , Na_2O , Na_2CO_3).

7.4.2 Brønsted and Lowry Theory

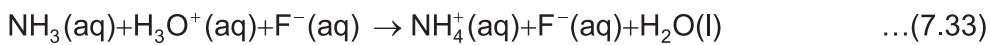
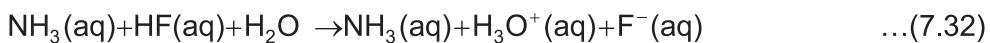
In 1923, Danish Chemist Johannes N. Brønsted and British Chemist Thomas M. Lowry independently addressed one of the limitations of Arrhenius theory and came up with a theory having wider applicability. According to them, an acid is defined as a species that can donate or transfer a proton (H^+) to another species, and a base is defined as a substance that can accept a proton from other species. The acid-base reactions then become just *proton-transfer* reactions between the donor and the acceptor; there is no requirement of water as the solvent. Thus, according to this theory, molecule or ion capable of donating or transferring a proton is an acid, while any molecule or ion that can accept a proton is a base. In other words, the definition applies to protonic systems. Let's take some examples

An acid contains at least one ionisable H atom, and a base contains an atom with a lone pair of electrons where the proton can bind.

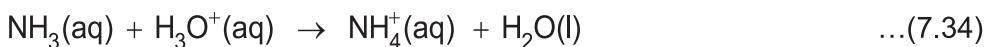
The reaction between ammonia (NH_3) and hydrogen fluoride (HF) in gaseous phase can be written as



Here, HF acts as an acid (as it donates or transfers a proton) and NH_3 acts as a base (as it accepts a proton). You may note in this example that there is no role of a solvent. However, the theory is applicable for aqueous systems also. Let's take the same example in aqueous medium. The reaction between ammonia and HF in aqueous medium can be written as

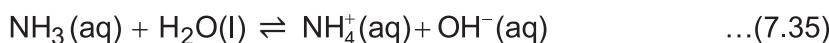


Omitting F^- ions on both sides in Eq. (7.33) we get



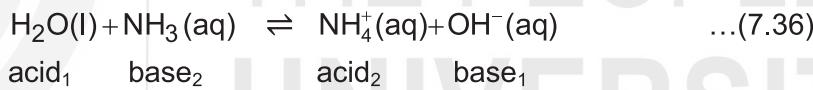
A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the gain or loss of a proton.

This reaction explains the basic nature of ammonia in terms of it accepting a proton from hydronium ion, which was formed by donation of a proton by HF to H₂O. Thus, in this reaction *the solvent (water) plays the role of a mediator in the transfer of proton from HF to ammonia*. It takes a proton from HF to form hydronium ion Eq. (7.32) and then transfers the same to ammonia molecule to form ammonium ion Eq. (7.34). Further, you may note that according to Brønsted-Lowry theory, in any acid-base equilibrium both forward and reverse reactions involve proton transfers. Let us consider the reaction of NH₃ with H₂O.

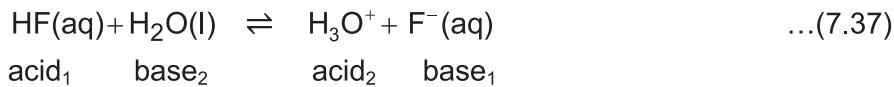


Here, in the forward reaction NH₃ behaves as a base as it accepts the proton and H₂O is acting as an acid by transferring its proton to ammonia molecule. In the reverse reaction NH₄⁺ ion acts as the acid and OH⁻ ion behaves as a base. When an acid (H₂O here) donates or transfers its proton to another species the remaining part of the acid becomes a base (OH⁻ here) and is called **conjugate base** of the acid. Similarly, when a base (NH₃ here) accepts a proton from another species it becomes an acid (NH₄⁺ here) and is called **conjugate acid** of the base. The species NH₄⁺ and NH₃[or H₂O and OH⁻] form a **conjugate acid-base pair** and is indicated by a diagonal line e.g., NH₄⁺/NH₃. The acid in such a pair is called conjugate acid of the base, whereas the base is the conjugate base of acid.

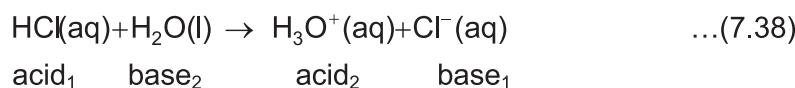
It is important to note that, in the equilibrium reaction, the members of each conjugate acid-base pair are designated by the same numerical subscript as shown below.



The position of the equilibrium is determined by the relative strengths of the acids and bases involved in the reaction. Let us take the example of ionisation of hydrogen fluoride in water to understand it. The equilibrium can be given as



In this case, the H⁺ ions obtained from the ionisation of HF molecule can be accepted either by F⁻ ions or by H₂O molecules. If the water molecules accept the proton, the reaction goes in the forward direction. On the other hand if F⁻ ions take the proton it makes the reaction go to left. It is experimentally found that the equilibrium is slightly towards the left; this indicates that the F⁻ ion is a stronger base than H₂O. Let's take another example, say dissolution of HCl in water.



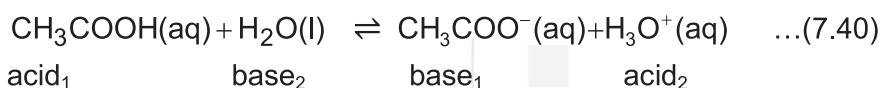
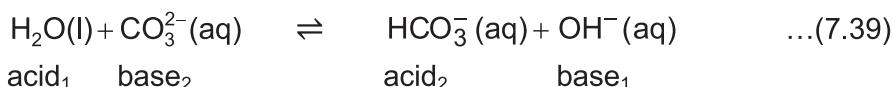
In this case, the hydrogen ions produced from the ionisation of HCl can be accepted either by H₂O molecules or by Cl⁻ ions. As we know that HCl is

completely ionised in dilute aqueous solution i.e., the reaction goes to completion in the forward direction. This means that Cl^- ion is a much weaker base than H_2O . What do we infer from these two examples?

Yes, you are right. We can infer that *in a conjugate acid-base pair a weaker acid has a stronger conjugate base whereas a stronger acid has a weaker conjugate base.*

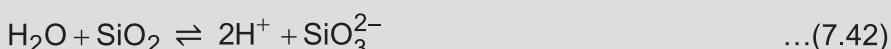
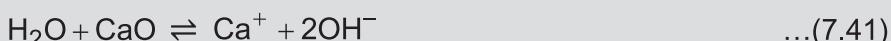
In a conjugate acid-base pair a weaker acid has a stronger conjugate base whereas a stronger acid has a weaker conjugate base.

As indicated above, according to the Brønsted and Lowry concept an acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind. In case the substance has an ionisable proton as well as a lone pair of electrons, it may behave either as an acid or as a base, depending on the other species in reaction. Water (H_2O) is an interesting molecule with these features; let us look at the following two examples



You may note here that in the first case H_2O is acting as an acid by donating a proton whereas in the second case it behaves as a base by accepting the proton. Such a substance that can behave as an acid as well as a base is called an **amphoteric substance**.

Similar to the Brønsted- Lowry concept involving proton transfer, another concept was proposed by German Chemist Hermann Lux in 1939 which was extended by H. Flood around 1947. It involved transfer of oxide ion in the acid- base reactions. According to **Lux-Flood definition** *an acid is defined as substance that is an oxide acceptor and base is an oxide donor.* This definition covers non-protonic systems, for example,



According to Lux-Flood definition an acid is defined as substance that is an oxide acceptor and base is an oxide donor.

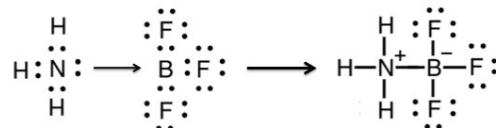
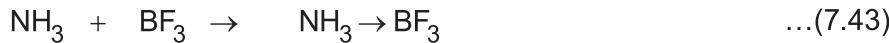
Here, CaO donates oxide therefore, it is a basic oxide whereas SiO_2 is an oxide acceptor and hence it is an acidic oxide.

You would have realized that the Brønsted- Lowry concept has a wider applicability than the Arrhenius concept, as it does not depend on the nature of solvent. However, even Brønsted-Lowry theory has a limitation that it is applicable for protonic systems only as it emphasizes the involvement of a proton. Further still, there are substances whose acid-base behaviour cannot be explained either by Arrhenius or Brønsted-Lowry theories. For example, AlCl_3 that does not contain a hydrogen atom but behave as an acid or Na_2CO_3 , which neither has OH nor accepts a proton but behaves as a base.

7.4.3 Lewis Theory

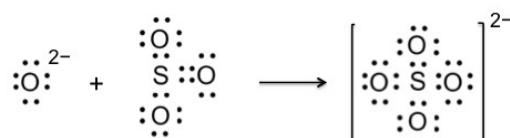
In 1923 G. N. Lewis proposed a yet another theory of acids and bases that has even broader applicability. It does not limit to systems involving H^+ or OH^- ions

but extends even to the reactions in gases and in solids. He defined an acid as a species (an atom, molecule or an ion) that can form a covalent bond by accepting an electron pair from another species, and a base as a species that can form a covalent bond by donating an electron pair to another species. Such acids and bases are called **Lewis acids and bases**. Lewis acids are species with vacant orbitals that can accommodate the electron pairs and Lewis bases are species that have lone-pair of electrons available for sharing. Let us take an example



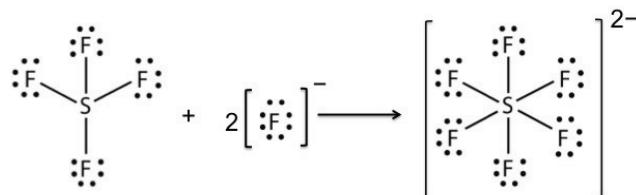
Lewis base Lewis acid

In this case the lone pair is donated by ammonia (base) and is accepted by electron deficient molecule BF_3 (acid). This reaction can be seen as a molecule with incomplete octet (BF_3) accepting a lone pair of electrons and completing its octet. In the following reaction, SO_3 is the Lewis acid that accepts the electron pair provided by oxide ion, and completes the octet of electrons on sulphur atom.



Lewis base Lewis acid

Sometimes a molecule or an ion may expand its octet to accept an electron pair. For example, in the reaction between SiF_4 and F^- ions to give SiF_6 , SiF_4 (Lewis acid) accepts two lone pairs of electrons from two F^- ions (Lewis bases) to give SiF_6^{2-} . Here, silicon expands its octet to accommodate six fluoride ions. You may note here that in SiF_6^{2-} silicon atom has twelve electrons around it.



Lewis acid Lewis base

The product of a Lewis acid– Lewis base reaction is called an **adduct** (or addition compound). You know that a covalent bond formed by the donation of a pair of electrons by an electron rich species to an electron deficient species is called a coordinate covalent bond. Thus, in an adduct the two species are linked by a **coordinate bond**. Having recalled different acid-base theories, why don't you test your understanding by solving the following simple self assessment questions?

SAQ 3

The species in the first column of the table given below act as acids. Write the corresponding conjugate bases in the second column.

Acid species	Conjugate base
HPO_4^{2-}	
HOCl	
PH_4^+	

SAQ 4

Identify the conjugate acid-base pairs in the following chemical reactions

- (a) $\text{SO}_3^{2-} + \text{NH}_4^+ \rightleftharpoons \text{HSO}_3^- + \text{NH}_3$
- (b) $\text{HS}^- + \text{CN}^- \rightleftharpoons \text{S}^{2-} + \text{HCN}$
- (c) $\text{F}^- + \text{HSO}_4^- \rightleftharpoons \text{HF} + \text{SO}_4^{2-}$

7.5 IONIC PRODUCT OF WATER, K_w

Pure water is generally considered to be a nonelectrolyte due to its negligibly small electrical conductivity. However, it does have a *non-zero* conductivity that indicates towards the presence of ions in pure water. Where do these ions come from? In order to answer this question; we recall an important property of water, viz., its amphoteric nature i.e., water can act as a weak acid as well as a weak base. In a sample of water a small number of water molecules donate a proton (thus acting as an acid), which is accepted by equal number of other water molecules (acting as bases) as shown below



As a consequence, a small concentration of H_3O^+ ions and OH^- ions is formed in a sample of water and this process is called **autoprotoysis (or autoionisation) of water**. The autoprotolysis of water indicates that water acts as an amphoteric substance even in the absence of any other substance. The equilibrium given in Eq. (7.46) is characterised by an equilibrium constant whose expression can be written as

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \dots(7.47)$$

As the degree of ionisation of water is very small i.e., very few water molecules are ionised, the concentration of H_2O remains unchanged (constant). The Eq. (7.47) can be rearranged to define a new constant K_w , as

$$K_{eq} \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad \dots(7.48)$$

This constant, K_w , is called the **ionic-product constant** of water. As defined, K_w is the product of the molar concentrations of H_3O^+ and OH^- ions in pure water sample at a given temperature. The value of K_w has been experimentally determined from the measurement of electrical conductivity of highly purified samples of distilled water at different temperatures and at 298 K its value has been found to be $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Using K_w we can find the concentrations of H_3O^+ and OH^- ions in water. As the autoprotolysis of water molecules give equal number of ions of each type, the concentrations of these ions is equal, we may, therefore, write

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2 = 1.0 \times 1.0^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad \dots(7.49)$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 1.0 \times 1.0^{-7} \text{ mol dm}^{-3} \quad \dots(7.50)$$

Thus, in pure water and in neutral aqueous solutions at 298 K

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 1.0^{-7} \text{ mol dm}^{-3} \quad \dots(7.51)$$

In acidic solutions this equality is disturbed and there are more hydronium ions than the hydroxide ions. Similarly, in basic solutions there would be an excess of OH^- ions. You must note here that hydronium ions and hydroxide ions are present in all aqueous solutions, and they are always in equilibrium with water molecules. *The autoprotolysis equilibrium discussed above applies to all aqueous solutions and the ionic-product equation holds for water.*

7.5.1 pH Scale

The concentration of H_3O^+ and OH^- ions in the aqueous solutions of acids and bases vary over a very wide range depending on the amount of acid or base added to water to get the solution. In order to quantitatively express the concentration of these ions especially in dilute solutions ($< 0.01 \text{ M}$) we need to use negative powers of 10 and it is quite inconvenient to handle these numbers. In 1909 a Danish botanist S.P.L. Sorenson, while working on brewing of beer, proposed a practical scale called **pH scale** for expressing the concentration or 'potential' of H^+ ions in aqueous solutions. He defined pH as the negative logarithm (to the base 10) of the molar concentration of hydrogen (we now use hydronium) ions in solution. That is,

$$\text{pH} = -\log_{10} [\text{H}^+] \quad \text{or} \quad -\log_{10} [\text{H}_3\text{O}^+] \quad \dots(7.52)$$

The letter p was derived from the German word 'Potenz' meaning power and the term in the square bracket represented the molar concentration of hydrogen ions. For example, if we have an aqueous solution in which the concentration of hydrogen ions is $1.0 \times 10^{-3} \text{ M}$, its pH can be calculated to be

$$\text{pH} = -\log_{10} [1 \times 10^{-3}] = -[-3] = 3$$

The basic logic of the scale was that by taking logarithm the numbers expressed as negative powers of 10, representing concentration of hydrogen ions, become simple negative numbers (e.g., $\log_{10} 10^{-3} = -3$), which are relatively easier to handle. However, to make it even better, the expression was multiplied by -1 so

that the concentration of hydrogen ions in aqueous solutions of acids and bases could be expressed in terms of simple positive numbers.

As stated above, Eq. (7.51); in pure water and in neutral solutions at 298 K, the concentration of hydronium ions would be $1.0 \times 10^{-7} \text{ mol dm}^{-3}$, which gives a pH value of 7.0.

$$\text{pH} = -\log_{10}[1 \times 10^{-7}] = -[-7] = 7$$

For acidic solutions the concentration of hydronium ions would be greater than $1.0 \times 10^{-7} \text{ mol dm}^{-3}$, which would give a pH of less than 7. On the other hand, in case of the basic solutions in which the concentration of hydronium ions would be less than $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ the pH would be more than 7. You may note here that the way pH is defined there is an inverse relationship between the concentration of hydrogen ions in the solution and its pH. Higher the concentration, lower the pH and vice-versa.

You should further note here that pH is not a physical property like pressure or volume it is merely a way of representing the concentration (which is a physical quantity) of hydronium ions in aqueous solutions. Secondly, you should also take note of the fact that like all equilibrium constants the value of K_w also depends on temperature and the value of 1.0×10^{-14} is at 298 K. At higher or lower temperatures than 298 K the value of K_w will be different. Accordingly, the concentration of hydronium ions in a water sample would be different. Say at 323 K where the value of $K_w = 5.47 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$, the concentration of hydronium ions in water would be $2.34 \times 10^{-7} \text{ mol dm}^{-3}$. This corresponds to a pH of 6.63. This means that pure water or a neutral aqueous solution would have a pH of 6.63 at 323 K.

A number of similar terms have been defined using the p notation, which means, 'the negative logarithm of'. The important and relevant ones are:

$$\text{pOH} = -\log_{10}[\text{OH}^-] \quad \dots(7.53)$$

$$\text{p}K_w = -\log_{10}K_w \quad \dots(7.54)$$

$$\text{p}K_a = -\log_{10}K_a \quad \dots(7.55)$$

$$\text{p}K_b = -\log_{10}K_b \quad \dots(7.56)$$

Of these the first two terms you can recognise and understand. You would learn about the other two in the next unit when we will deal with weak acids and bases. There is an important relationship between pH, pOH and p K_w . Let's workout the relationship by recalling the following expression:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \dots(7.48)$$

Taking logs and multiplying by -1 on both sides, we get

$$-\log K_w = -\log[\text{H}_3\text{O}^+] -\log[\text{OH}^-] \quad \dots(7.57)$$

$$\Rightarrow \text{p}K_w = \text{pH} + \text{pOH} \quad \dots(7.58)$$

Aqueous solutions at 298 K

Neutral solutions:

$$\text{pH}=7.0$$

Acidic solutions:

$$\text{pH} < 7.0$$

Basic solutions:

$$\text{pH} > 7.0$$

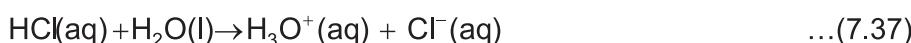
As you know that at 298 K the value of $K_w = 1.0 \times 10^{-14}$ which, gives the value of pK_w to be 14. Substituting it in Eq. (7.58) we get the following important expression (valid at 298 K)

$$\text{pH} + \text{pOH} = 14 \quad \dots(7.59)$$

This means that if we know the value of pH of a given solution at 298 K we can find its pOH value and vice versa by using the Eq. (7.59).

7.5.2 Calculation of pH

Let us take up some examples to learn about calculating pH values for aqueous solutions of strong acids and bases using the equations given above. Let's begin by calculating the pH value for 0.001 M aqueous solution of HCl. As you are aware, HCl is a strong acid so it would ionise completely in solution and we can write.



As we have 0.001 M HCl it will provide 0.001 M hydronium ions on complete ionisation. So the concentration of H_3O^+ ions would be $= 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ which can be used to calculate the pH. However, before attempting the calculation let us also consider the other source of hydronium ions in the solution i.e., autoprotolysis of water



If we assume the temperature to be 298 K then autoprotolysis of water is expected to provide $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ of hydronium ions. This number is much smaller ($1/10,000$) than $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ obtained from ionisation of HCl. This gets even smaller due to common ion effect because according to Le-Chatelier principle the hydronium ions obtained from the ionisation of HCl cause the autoprotolysis equilibrium to shift to the left and decrease the concentration of hydronium ions obtained from autoprotolysis of water.

In absence of HCl, $[\text{H}_3\text{O}^+]_{\text{water}}$ from autoprotolysis $= 1.0 \times 10^{-7} \text{ M}$

In presence of HCl, $[\text{H}_3\text{O}^+]_{\text{water}}$ from autoprotolysis $= << 1.0 \times 10^{-7} \text{ M}$

As the concentration of hydronium ions obtained from autoprotolysis of water is much smaller than that obtained from ionisation of HCl it can be ignored and we can calculate the pH based on the concentration of hydronium ions obtained from ionisation of HCl only. That is

$$\text{pH} = -\log_{10} [1 \times 10^{-3}] = -[-3] = 3$$

Let's go further and calculate the pH of a solution of HCl obtained by diluting

the above solution 100 times i.e., it has a concentration $= \frac{1 \times 10^{-3}}{100} = 1 \times 10^{-5} \text{ M}$

Proceeding as before we get:

Concentration of hydronium ions from ionisation of HCl $= 1.0 \times 10^{-5} \text{ M}$

Concentration of hydronium ions from autoprotolysis of water $= < 1.0 \times 10^{-7} \text{ M}$

If the concentration of a species from a minor source happens to be less than or equal to 5% of the concentration from a major source, then it can be ignored without causing appreciable change in the calculated value.

As the concentration of hydronium ions from autoprotolysis of water is less than 1% of that obtained from dissociation of HCl, we can again ignore it and calculate the pH based on the concentration of hydronium ions obtained from ionisation of HCl only. That is

$$\text{pH} = -\log_{10}[1 \times 10^{-5}] = -[-5] = 5$$

Now, if we go still further and dilute the HCl solution in question by another 100 times then what would be the pH? Will it be 7.0 as the concentration of HCl would be 1.0×10^{-7} M? Let's analyse. Proceeding as before, we get:

Concentration of hydronium ions from ionisation of HCl = 1.0×10^{-7} M

Concentration of hydronium ions from autoprotolysis of water $\sim 1.0 \times 10^{-7}$ M

Now since the concentration of hydronium ions from two sources are comparable we cannot ignore the hydronium ions obtained from autoprotolysis of water. We need to work out the total concentration of hydronium ions. As HCl is a strong electrolyte so we are sure about the concentration of hydronium ions from complete ionisation of HCl = 1.0×10^{-7} M. However, in order to calculate the amount of hydronium ions from autoprotolysis of water we need to solve the autoprotolysis equilibrium applying the common ion effect as shown below. We assume that the concentration of hydronium ions obtained from autoprotolysis of water = x

$\text{H}_2\text{O} (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$		
Concentration of ions from autoprotolysis of water	x	x
Concentration of H_3O^+ ions from ionisation of HCl	1.0×10^{-7}	0
Total H_3O^+ ion concentration	$[x + (1.0 \times 10^{-7})]$	x

Assuming the temperature to be 298 K, the following equation must hold for the aqueous solution.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad \dots(7.49)$$

Substituting the values from the table we get

$$[x + (1.0 \times 10^{-7})](x) = 1.0 \times 10^{-14}$$

On simplification we get a quadratic equation as follows,

$$x^2 + (1.0 \times 10^{-7})(x) - (1.0 \times 10^{-14}) = 0$$

$$\Rightarrow x^2 + (1 \times 10^{-7})x - (1 \times 10^{-14}) = 0$$

As you know that for a quadratic equation, $ax^2 + bx + c = 0$, the value of x can be obtained by the following expression

$$= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

So for our equation,

$$\begin{aligned}
 x &= \frac{-10^{-7} \pm [(10^{-7})^2 + (4 \times 1 \times 10^{-14})]^{1/2}}{2} \\
 &= \frac{-10^{-7} \pm [5 \times 10^{-14}]^{1/2}}{2} \\
 &= \frac{-10^{-7} \pm [2.24 \times 10^{-7}]}{2} \\
 &= \frac{1.24 \times 10^{-7}}{2} = 6.2 \times 10^{-8} \text{ M} \quad (\text{Ignoring the negative root})
 \end{aligned}$$

The total concentration of hydronium ions in the solution = Hydronium ions from ionisation of HCl + hydronium ions from autoprotolysis of water

$$\begin{aligned}
 &= (1.0 \times 10^{-7}) + (6.2 \times 10^{-8}) \\
 &= 1.62 \times 10^{-7} \text{ M} \\
 \Rightarrow \text{pH} &= -\log_{10}[1.62 \times 10^{-7}] = -[-6.79] = 6.79
 \end{aligned}$$

Having learnt about the calculation of pH values of the solution of an acid (hydrochloric acid) at different concentrations, let us learn about the calculation of pH of a solution of a base by taking an example.

Example 7.1: Calculate the pH of 0.010 M aqueous solution of NaOH at 298 K.

Solution: Since NaOH is a strong base; it will fully ionise in the solution to give Na^+ and OH^- ions as given below



The concentration of hydroxide ions would be

$$[\text{OH}^-] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

From Eq. 7.48 we know that,

$$\begin{aligned}
 K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] \\
 \Rightarrow [\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]}
 \end{aligned}$$

Substituting the values at 298 K,

$$\begin{aligned}
 \Rightarrow [\text{H}_3\text{O}^+] &= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.00 \times 10^{-2} \text{ mol dm}^{-3}} \\
 &= 1.00 \times 10^{-12} \text{ mol dm}^{-3}
 \end{aligned}$$

$$\text{pH} = -\log(1.00 \times 10^{-12}) = -(-12) = 12$$

Alternatively, we can first use the concentration of hydroxide ions to find pOH and then use Eq. (7.59) to find out the value of pH, i.e.,

$$\text{pOH} = -\log(1.00 \times 10^{-2}) = -(-2) = 2$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 2 = 12$$

Thus the pH of the solution would be 12.

Having learnt about the calculation of pH for aqueous solutions of acids and bases, solve the following SAQs to gauge your understanding of these.

SAQ 5

Calculate the pH of 2×10^{-3} M aqueous solution of hydrochloric acid.

SAQ 6

What would be the pH of the resulting solution if 100 cm^3 of 2×10^{-3} M hydrochloric acid solution is mixed with 150 cm^3 of 2×10^{-3} M solution of sodium hydroxide at 298 K?

7.6 SUMMARY

In this introductory unit on ionic equilibrium we started by discussing the nature of aqueous solutions in terms of their electrical conductivity based on the nature of the solute. Herein, we introduced the concept of an electrolyte and defined it to be a substance, which when dissolved in water gives an electrically conducting solution. The electrolytes, which completely dissociate or ionise in aqueous solutions are called strong electrolytes and are highly conducting. On the other hand, the electrolytes that are partially ionised are called weak electrolytes and their solutions have low electrical conductivity. We also discussed the factors affecting the ionisation of weak electrolytes. These happen to be the nature of solvent, temperature, presence of common ions and dilution. The variation of degree of ionisation of weak electrolytes with concentration was expressed in terms of Ostwald's dilution law. According to this law "The degree of ionisation of a weak electrolyte in a solution is directly proportional to square root of dilution".

After the discussion on electrolytes, their types and the factors affecting their behaviour we reviewed different concepts of acids and bases. We started by recalling Arrhenius concept, according to which an acid is defined as a species that generates a hydrogen ion in water and a base as the species that provides hydroxide ions in water. Though a simple concept, it has limited applicability as it is valid only for aqueous solutions and does not include

species that do not have a hydrogen or OH. On the other hand, in Brønsted and Lowry concept the acids and bases are defined in terms of transfer of protons. The species transferring the proton is called an acid and the one accepting it is called a base. According to Brønsted-Lowry concept in any acid-base equilibrium both forward and reverse reactions involve proton transfers. The species on either side of the equilibrium are related as conjugated acid-base pairs. A stronger acid has a weaker conjugate base and vice versa. The Lewis concept, which we discussed later, describes acid-base behavior in terms of donation/ acceptance of a lone pair of electron from one species to another; the donor being a base and the acceptor an acid.

We then discussed about the consequences of the amphoteric nature of water. It was stated that in a sample of pure water some molecules donate a H⁺ ion whereas an equal number of others accepts the same. This leads to the formation of hydronium and hydroxide ions and the process is called autoprotolysis of water. The product of the concentrations of hydronium ions and hydroxide ions in an aqueous solution is called ionic product constant of water and has a unique value at a given temperature. Using autoprotolysis of water we introduced the concept of pH which is a scale used for expressing the concentrations of H⁺ ions in aqueous solutions. The pH is defined as the negative logarithm (to the base 10) of the molar concentration of hydrogen (or hydronium) ions in solution. We also explained the procedure to calculate the pH of aqueous solutions of strong acids and bases with the help of examples.

7.7 TERMINAL QUESTIONS

1. Define an electrolyte and differentiate between weak and strong electrolytes.
2. List different factors that affect the ionisation of weak electrolytes.
3. Outline the drawbacks of Arrhenius theory of acids and bases.
4. In the following reactions, label each species as an acid or a base. Also identify the conjugate acid-base pairs in these reactions.
 - a. $\text{HSO}_4^-(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{NH}_4^+(\text{aq})$
 - b. $\text{HPO}_4^{2-}(\text{aq}) + \text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{NH}_3(\text{aq})$
5. In a conjugate acid-base pair a stronger conjugate acid has a weaker conjugate base and vice-versa. Explain with the help of suitable examples.
6. What is an amphoteric substance? With the help of suitable examples show that water is an amphoteric substance.
7. In the following reactions, identify the Lewis acid and Lewis base.
 - a. $\text{SnCl}_4 + 2\text{Cl}^- \rightarrow \text{SnCl}_6^{2-}$
 - b. $\text{BBr}_3 + :\text{AsH}_3 \rightarrow \text{BBr}_3 \leftarrow \text{AsH}_3$

8. What is pH? Calculate the pH of a solution of hydrochloric acid having a concentration of 2×10^{-5} M.
9. Calculate the pH of a solution prepared by mixing 100 cm^3 of 0.001 M HCl and 300 cm^3 of 0.020 M NaOH at 298 K.

7.8 ANSWERS

Self-Assessment Questions

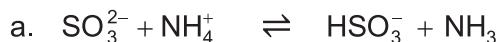
1. Ionisation and dissociation are closely related processes associated with the dissolution of electrolyte in water to make a solution. These are often used interchangeably; however, there is a minor difference. When an ionic electrolyte e.g., NaCl which consists of ions packed in a crystal lattice is dissolved, the ions dissociate from one another and go into solution. Such a process is called dissociation. On the other hand, when we dissolve a molecular electrolyte e.g., acetic acid, the electrolyte molecules ionise and produce ions in solution. Such a process is called ionisation. Thus, in dissociation the ions already present in the electrolyte become free in solution whereas in ionisation the ions are formed from molecular electrolyte under the influence of the solvent.
2. According to Ostwald's dilution law, "The degree of ionisation of a weak electrolyte is directly proportional to the square root of dilution". For a weak electrolyte, the degree of ionisation (α), the concentration (c), and the equilibrium constant (K) are related as $\alpha = \sqrt{K/c}$.

As the concentration of a solution containing certain amount of electrolyte is related inversely with the volume of the solution containing one mole of the solute (dilution) we can write $\alpha = \sqrt{KV}$. Thus, as the volume (V) of the solution containing a given amount of weak electrolyte increases the degree of ionisation of the electrolyte increases.

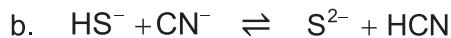
3. The conjugate bases of given acids are as under:

Acid species	Conjugate base
HPO_4^{2-}	PO_4^{3-}
HOCl	ClO^-
PH_4^+	PH_3

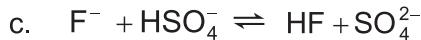
4. The conjugate acid-base pairs in given reactions are as under:



Conjugate acid/base pairs: $\text{NH}_4^+/\text{NH}_3$ and $\text{HSO}_3^-/\text{SO}_3^{2-}$

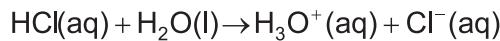


Conjugate acid/base pairs: HCN/CN^- and $\text{HS}^-/\text{S}^{2-}$



Conjugate acid/base pairs: $\text{HSO}_4^- / \text{SO}_4^{2-}$ and HF / F^-

5. HCl is a strong acid so it would ionise completely in solution and we can write.



As we have 2×10^{-3} M HCl, the concentration of H_3O^+ ions would be $= 2.0 \times 10^{-3}$ mol dm $^{-3}$. In addition to this we would have about 1×10^{-7} mol dm $^{-3}$ of hydronium ions from autoprotolysis of water. Since this number is negligibly small as compared to the concentration of hydronium ions obtained from ionisation of HCl, we calculate the pH by using the concentration of hydronium ions obtained only from hydrochloric acid i.e., 2.0×10^{-3} M

$$\text{Therefore, } \text{pH} = -\log_{10} [2 \times 10^{-3}] = -[-2.70] = 2.70$$

6. When we add 150 cm^3 of 2×10^{-3} M sodium hydroxide solution to 100 cm^3 of 2×10^{-3} M hydrochloric acid solution all the hydrochloric acid would be neutralised by 100 cm^3 of NaOH and there will be an excess of 50 cm^3 of 2×10^{-3} M sodium hydroxide that will be present in a total volume of 250 cm^3 . Therefore, we can calculate the final concentration of sodium hydroxide using the formula $M_1V_1 = M_2V_2$.

$$M_2 = \frac{M_1V_1}{V_2}$$

Substituting the values,

$$M_2 = \frac{0.002 \times 50}{250} = 0.0004 \text{ M}$$

Since NaOH is a strong base it is fully ionised to give Na^+ and OH^- ions, i.e., the concentration of hydroxide ions would be

$$\Rightarrow [\text{OH}^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$$

we know that,

$$[K_w] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

Substituting the values at 298 K,

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{4.00 \times 10^{-4} \text{ mol dm}^{-3}}$$

$$= 2.50 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log (2.50 \times 10^{-9}) = -(-8.60) = 8.60$$

Thus, the pH of the given solution would be 8.60

Terminal Questions

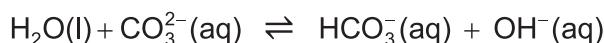
1. An electrolyte may be defined as a substance which when dissolved in water gives an electrically conducting solution. The electrolytes which completely dissociate or ionise in aqueous solutions e.g., sodium chloride are called strong electrolytes and have high electrical conductivity. On the other hand, the electrolytes that are partially ionised, e.g., acetic acid are called weak electrolytes and have low electrical conductivity.
2. The following factors affect the degree of ionisation of weak electrolytes:
 - i. Nature of solvent
 - ii. Temperature
 - iii. Presence of common ions
 - iv. Dilution
3. The following are some of the limitations of Arrhenius theory of acids and bases:
 - It is applicable for aqueous solutions only and does not explain the acid-base behaviour in non-aqueous solvents or in gaseous systems.
 - It does not explain the acidic behaviour of substances that lack hydrogen e.g., AlCl_3 or the basic character of substances that lack OH e.g., NH_3 .
4. The acids and bases and the conjugate acid-base pairs in given reactions are as under:
 - a. $\text{HSO}_4^- + \text{NH}_3 \rightleftharpoons \text{SO}_4^{2-} + \text{NH}_4^+$
 acid₁ base₂ base₁ acid₂
 The conjugate acid-base pairs are $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{NH}_4^+/\text{NH}_3$
 - b. $\text{HPO}_4^{2-} + \text{NH}_4^+ \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{NH}_3$
 base₁ acid₂ acid₁ base₂
 The conjugate acid-base pairs are $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{NH}_4^+/\text{NH}_3$
5. In Brønsted and Lowry concept the acids and bases are defined in terms of transfer of protons. For example, when we dissolve ammonia in water, the following equilibrium is established.



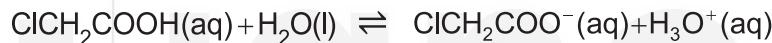
Here ammonia accepts a proton from water and acts as a base whereas water acts as an acid in the forward reaction. In the reverse reaction ammonium ion donates a proton to hydroxide ion and acts as an acid; the hydroxide ions act as a base. Here, NH_4^+ ions and NH_3 constitute a conjugate acid-base pair. Similarly, H_2O and OH^- ions form a conjugate acid-base pair.

As the reaction proceeds to a good extent in the forward direction we can say that water is a stronger acid than ammonium ion. There are two bases in the reaction (NH_3 and OH^-). The reaction proceeding in the forward direction means that the proton donated by water is accepted by ammonia in preference to hydroxide ion. That is ammonia is a stronger base than hydroxide ion. Thus, we can say that the conjugate base (OH^-) of a stronger acid (H_2O) is a weaker base. Similarly, the conjugate acid (NH_4^+) of a stronger base (NH_3) is a weaker acid.

6. A substance that can behave as an acid or as a base depending on other substance in the reaction is called an amphoteric substance. Water is a common example of amphoteric substances. In the following reaction



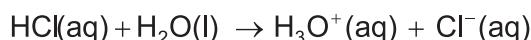
Water acts as an acid by donating a proton to carbonate ions. On the other hand, in the reaction given below, water acts as a base by accepting a proton from chloroacetic acid.



7. a. In this reaction SnCl_4 is the acid whereas Cl^- ions act as base.
- b. In this reaction BBr_3 is the acid whereas AsH_3 acts as base.
8. It is a scale for expressing the concentrations of H^+ ions in aqueous solutions. It is defined as the negative logarithm (to the base 10) of the molar concentration of hydrogen (or hydronium) ions in solution. That is,

$$\text{pH} = -\log_{10}[\text{H}^+] \text{ or } = -\log [\text{H}_3\text{O}^+]$$

HCl is a strong acid so it would ionise completely in solution and we can write.



As we have 2×10^{-5} M HCl it will provide 2×10^{-5} M hydronium ions on complete ionisation i.e., the concentration of H_3O^+ ions in the solution = 2.0×10^{-5} mol dm⁻³. In addition to this we would have about 1×10^{-7} mol dm⁻³ of hydronium ions from autoprotolysis of water. However, due to common ion effect of the hydronium ions obtained from ionisation of HCl the autoprotolysis of water gets suppressed and the concentration of hydronium ions from this source gets further reduced.

Under these conditions, the concentration of hydronium ions from autoprotolysis of water is negligibly small as compared to the hydronium ions obtained from ionisation of hydrochloric acid. So we calculate the pH of the solution by using the concentration of hydronium ion obtained from ionisation of HCl only i.e., = 2.0×10^{-5}

$$\text{Therefore, pH} = -\log [2 \times 10^{-5}] = -[-4.70] = 4.70$$

9. The given solution has hydrochloric acid as well as sodium hydroxide so the two would neutralise each other. We need to find out the final composition of the solution before calculating the pH. To begin with, we can calculate the amounts of HCl and NaOH individually.

HCl has a concentration of 0.01 M which means its has 0.01 moles of HCl in 1000 cm³ or $0.01 / 1000 = 1 \times 10^{-5}$ moles of HCl per cm³ of the solution

As the volume of HCl is 100 cm³ so there are $100 \times 1 \times 10^{-5}$ moles = 1×10^{-3} moles of HCl = 0.001 moles of HCl in the solution.

Similarly, we can calculate the number of moles of NaOH in the solution to be

$$= \frac{0.02}{1000} \times 300 = 0.006 \text{ moles}$$

Of these, 0.006 moles of NaOH, 0.001 moles would be used to neutralise all the HCl and there will be an excess of $0.006 - 0.001 = 0.005$ moles of NaOH. Now, these 0.005 moles are present in a total volume of 400 cm³

$$\Rightarrow \text{Concentration of NaOH} = \frac{0.005}{400} \times 1000 = 0.0125 \text{ M} = 1.25 \times 10^{-2} \text{ M}$$

Since NaOH is a strong base it is fully ionised to give Na⁺ and OH⁻ ions.



$$\Rightarrow [\text{OH}^-] = 1.25 \times 10^{-2} \text{ mol dm}^{-3}$$

we know that $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

Substituting the values at 298 K,

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.25 \times 10^{-2} \text{ mol dm}^{-3}} = 8.0 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log[8.0 \times 10^{-13}] = -[-12.1] = 12.1$$

Thus, the pH of the given solution would be 12.1.